

Surfactant-Assisted Coal Liquefaction

Gregory S. Hickey and Pramod K. Sharma
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

Abstract

Obtaining liquid fuels from coal which are economically competitive with those obtained from petroleum based sources is a significant challenge for the researcher as well as the chemical industry. Presently, the economics of coal liquefaction are not favorable because of relatively intense processing conditions (temperatures of 430 °C and pressures of 2200 psig), use of a costly catalyst, and a low quality product slate of relatively high boiling fractions. The economics could be made more favorable by achieving adequate coal conversions at less intense processing conditions and improving the product slate. A study has been carried out to examine the effect of a surfactant in reducing particle agglomeration and improving hydrodynamics in the coal liquefaction reactor to increase coal conversions. A series of coal liquefaction experiments with surfactant addition were conducted in a stirred batch autoclave with typical coal-solvent mixtures at temperatures from 300 to 375 °C and pressures from 1500 to 1800 psig. The treated products were analyzed for overall conversion and the distribution of the converted products into lighter and heavy oil fractions, respectively. The results indicate a significant increase in coal conversions due to surfactant addition at all processing conditions. The analysis also indicates an upgrading of the product slate for temperatures not exceeding 350 °C. These results imply a significant cost savings (and hence improved economics) by use of a disposable surfactant in coal liquefaction.

Introduction

The liquefaction of coal is a promising technology for producing alternate fuels that may eventually replace petroleum based fuels. This technology has the implication toward the goal of attaining self-sufficiency in the Nations energy needs. However in order to make coal liquefaction technology competitive with existing energy sources, high carbon conversion without extensive processing of the coal is desired. It has long been known that the operating conditions (such as solvent type and structure, the hydrogen to carbon (H/C) ratio, temperature, etc.) play a significant role in the dissolution and reaction of the organic matter in the coal. The possible effects of lowering the viscosity and surface tension of the liquid phase in the reactor have mostly been speculated upon but not systematically investigated. Further, the research emphasis in coal liquefaction has recently shifted away from intensive processing to maximize liquid yields toward milder processing to obtain a more economically attractive slate of products. This present work studies the effect of adding a surfactant to the coal liquefaction process in order to explore the possibility of designing an efficient process operable under less intensive conditions and improve distillate quality yields.

A Phase I study¹ using the surfactant approach for milder processing in liquefaction was completed at the Jet Propulsion Laboratory (JPL) in December 1990. This study, though preliminary and of a limited scope, identified sodium lignosulfonate as the surfactant additive which appeared most promising based upon viscosity tests. A few coal liquefaction autoclave test runs carried out with a small amount of the lignosulfonate additive showed an increase in light soluble solids. These preliminary tests also indicated a possible increase in the liquid yields. The present work effort relates to an investigation of surfactant-assisted coal liquefaction with the objective of quantifying the enhancement in liquid yields and the product quality.

The structure of coal has been investigated by many researchers and it is generally agreed to consider coal as a highly crosslinked polymer, which consists of a large number of stable aggregates connected by relatively weak hydrogen bond crosslinks. Coal fragments typically disperse poorly in nonpolar and mildly polar solvents, and tend to agglomerate into aggregates of high molecular weights. The approach was to add a surfactant with an "asphaltene-like" structure to better disperse the particles and prevent them from aggregating. Sodium lignosulfonate surfactant was chosen because it is an oil-compatible colloidal surfactant that is commercially available as an inexpensive by-product from waste paper and pulp processing. At mild processing temperatures it readily disperses in hydrocarbon solvents as molecular units. It is typically used in industry as a dispersion agent for solids, and as an oil-water emulsion stabilizer with free aromatic, cyclic, primary and secondary alcoholic carboxylate groupings.

Experimental

The effect of surfactant addition on coal liquefaction was studied in a series of batch autoclave reactor experiments. The surfactant assisted coal liquefaction experimental reactor system consists of a Parr series 4500 autoclave and accessories. The reactor consists of a one liter stainless steel pressure vessel with a maximum operation pressure of 1900 psig at 375 °C. The reactor contents are mixed by a belt driven stirrer with a six blade turbine-type impeller. The reactor system has gas lines and flow valves for nitrogen and hydrogen, and a vent line with burst reservoir. For safety, the reactor has a pressure relief valve rated at 1910 psig, and a burst valve rated at 2200 psig. Pressure is measured by a 3000 psig pressure gauge, and temperature by a thermocouple inserted into a thermowell within the reactor. Temperature is controlled by an automatic temperature controller.

The coal being used in this study is Illinois # 6 obtained from the Penn State Coal Data Bank (PSCD) with PSCD designation DECS-2. The coal particle size is -60 mesh and is stored in a sealed, dry container. The coal is used in as-received condition. The solvent used is SRC-2 recycle solvent obtained from Hydrocarbon Research Inc. (HRI). The surfactant is sodium lignosulfonate obtained from Pfaltz and Bauer (Catalogue No. S05950).

The sodium lignosulfonate surfactant was added in concentrations of 0.0, 0.5, 1.0 and 2.0 Wt % additions based on total slurry. The processing temperatures were from 300 to 375°C, with hydrogen pressure at 1800 psig, and a processing time of 1 hour was used on the majority of runs. Selected experiments were conducted with

time as a variable and at a lower pressure. Conversions are reported on a moisture and ash free (MAF) basis and were determined by a mass balance of the amount of coal derived liquid produced and coal slurry filter cake that could be extracted by tetrahydrofuran (THF) after processing. The experimental run procedures and analysis scheme have been presented in detail previously^{2,3}. The procedures have been developed over the last year to produce consistent and reproducible experimental results.

Coal Conversions

The product slurry usually separates into two fractions, the top fraction being mostly liquid, while the bottom fraction contains the major part of the solids. The top fraction is decanted, filtered and put in a collection vessel, and the remaining wet solids are vacuum filtered for 15 minutes to remove the filterable liquids from the filter cake. The filtration is conducted with a buchner funnel with 5 micron pore size filter paper. The filtered liquid is added to the original filtrate. The filtrate and the filter cake are weighed and the mass balance closure during the filtration step is verified.

The filter cake is subjected to a series of extractions to determine the light oil, asphaltenes and preasphaltene fractions. The solvents used for successive extractions are hexanes, toluene and tetrahydrofuran (THF), respectively. All solvents are reagent grade. For the extraction, 10 grams of filter cake are added to 30 ml of hexanes, stirred, and allowed to sit overnight. The slurry is then vacuum filtered using a conical funnel and 2.5 micron pore size filter paper (Whatman 42). The mixture is washed with solvent until the filtrate is clear. The remaining solvent is removed by heating the filter cake in an oven maintained at a temperature of about 100 °C for 4 to 8 hours. The dried filter cake is weighed and then mixed with 30 ml of toluene for the toluene extraction and the extraction procedure is repeated and the sample is dried at 125 °C for 4 to 8 hrs. The final filter cake is then extracted with THF. At the completion of the THF extraction, the THF insoluble solids are dried 16 hrs at 100 °C in air to drive off any residual solvent before a final weight is determined.

Coal conversions were obtained based on the conversion of the moisture and ash free (MAF) carbonaceous material to either the coal-derived liquid directly or the fraction that is soluble in solvents used in the extractions with the filter cake. The conversion was obtained using the relationship:

$$\text{MAF Conversion} = (W_{\text{init}} - W_{\text{fin}})/W_{\text{init}}$$

where W_{init} is the initial weight of the coal on moisture and ash-free basis subjected to liquefaction and W_{fin} is the final weight of the carbonaceous residue obtained from the treated slurry that is not soluble in hexanes, toluene or THF. Note that W_{fin} is to be corrected by subtracting the ash in the initial sample as well as subtracting the insoluble part of the surfactant in the runs where surfactant was added.

To validate that this extraction procedure extracts only reacted coal, the extraction sequence was performed on as-received Illinois #6 coal. The pseudo-conversion for raw coal (after successive washes with hexane, toluene, and THF) was similarly determined and was found to be only about 2.0 percent. Careful attention was

paid to minimize material losses at each processing and analysis step, and as a result, the mass balances closed to within 3 percent.

in order to characterize the liquid obtained as the filtrate, 50 ml of the filtrate are removed for atmospheric distillation using the procedure outlined in ASTM D 246-89⁴. Distillation fractions are taken for the following cuts: room temperature to 210 °C, 210 to 270 °C, 270 to 300 °C, and residual bottoms. This distillation gives a measurement of the lower-temperature boiling point fractions.

Results

Table 1 shows overall conversion results for processing runs that were completed with 1 hour processing time with Illinois #6 coal and varying amounts of sodium lignosulfonate surfactant. The pressures were 1800 psig hydrogen unless noted. The uncertainty in the conversion values is estimated to be less than 3 percent. From an examination of the data presented in above table some noteworthy trends are apparent. One trend is the dependence of the conversion upon operating temperature with and without the surfactant. This dependence is illustrated in Figure 1. Note that the surfactant addition increases the coal conversions by about 10 to 20 percent, generally increasing with temperature with the largest absolute increase occurring at the temperature of 350 °C. As seen in Table 1, only a small amount of surfactant is required to increase conversion.

Table 1: Test matrix results of Illinois #6 coal conversion (MAF basis) processed for one hour with varying amount of sodium lignosulfonate surfactant.

| Temperature | H ₂ Pressure (Psig) | surfs.cmnt Concentration | | | |
|-------------|-----------------------------------|--------------------------|------------|----------|--------------|
| | | 0% | 0.5 % | 1.0 % | 2.0 % |
| 300 °C | 1800 | 21.4 % | 24.7 % | 24.6 % | 24.5 % |
| 325 °C | <1800 | | | | 24.2 % (A) |
| 325 °C | 1800 | 25.4 % | 29.8 % | 36.5 % | 29.2% |
| 350 °C | <1800 | | 65.9 % (B) | | 60.0 % (C) |
| 350 °C | 1800 | 54.4 0/0 | | 62.5 7%0 | 63.1 % |
| 375 °C | <1800 | 77.0 % (B) | | | 82.5 0/0 (C) |
| 375 °C | 1800 | 83.1 % | 86.0?40 | 85.9 % | 87.4 % |

Notes: A: 1050 Psig, B: 1300 Psig, C: 1500 Psig

Detailed results of the distillation cuts are presented elsewhere^{3,5}, so only general trends will be discussed here. One important trend is that the addition of the surfactant increases the amount of the light distillates at processing temperatures up to

375 °C.. Light boiling fractions are defined as having a boiling point less than 300 °C. This trend is illustrated in Figure 2, which compares the 2.0 %surfactant addition versus the 0 % case.

It was also noted that the production of preasphaltenes increases with processing temperature. The production of preasphaltenes was determined from the THF extraction that succeeded the hexane and toluene washes. This is illustrated in Figure 3. There is a greater increase in the amount of preashaltenes with the addition of the surfactant. This would appear to be due to high molecular weight fragments (preasphaltenes) from the coal entering the liquid product.

As expected, the conversion of the coal showed a strong dependence on processing time. This trend is illustrated in Figure 4. The addition of the surfactant increases the rate of conversion at shorter processing times compared to the case without surfactant. At longer processing times, the coal processed without surfactant approached the conversion of the surfactant added processing runs. The maximum MAF conversion for Illinois #6 coal in a catalytic reactor with long processing times approaches 95 %. Complete conversion is not achieved due to nonreactive carbon in the coal macerals.

A detailed analysis of the coal filtercake and filtrate products was conducted to help determine the possible mechanism associated with the surfactant on improving the liquefaction of the coal in this study. The analysis is presented elsewhere, so only the highlights will be reviewed. The analysis included FTIR analysis of the filtercakes, filtrates and residues, proton and ^{13}C NMR of selected filtrates and GC/MS of filtercake extracts to determine the chemical composition of the liquefaction products in reaction runs with and without the surfactant. The primary results show that the addition of the surfactant increases both the amount and constituent species of light oils, asphaltenes, and preashaltenes, as compared to equivalent processing runs without surfactant. Physical examination of the processed coal suggests that the addition of the surfactant opens up the crosslinked structure of the coal, allowing more surface area to react.

Discussion

The batch autoclave tests indicate a significant increase in overall coal conversions due to the surfactant addition at all operating temperatures in the range from 300 to 375°C. Coal liquefaction conversion has a strong dependence on temperature. Below 350 °C there is only a small amount of conversion. As expected, increasing temperature increased the rate of conversion. Within the pressure range evaluated in this study, there was a weak dependence on hydrogen pressure. This work was conducted at 1800 psig hydrogen as the maximum pressure due to equipment limitations, whereas Industrial processes have operated at 2200 psig hydrogen. There is only a need for a small amount of surfactant to show a significant increase in conversion. Adding additional surfactant from 0.5 to 2.0% concentration produced only a small additional increase in conversion.

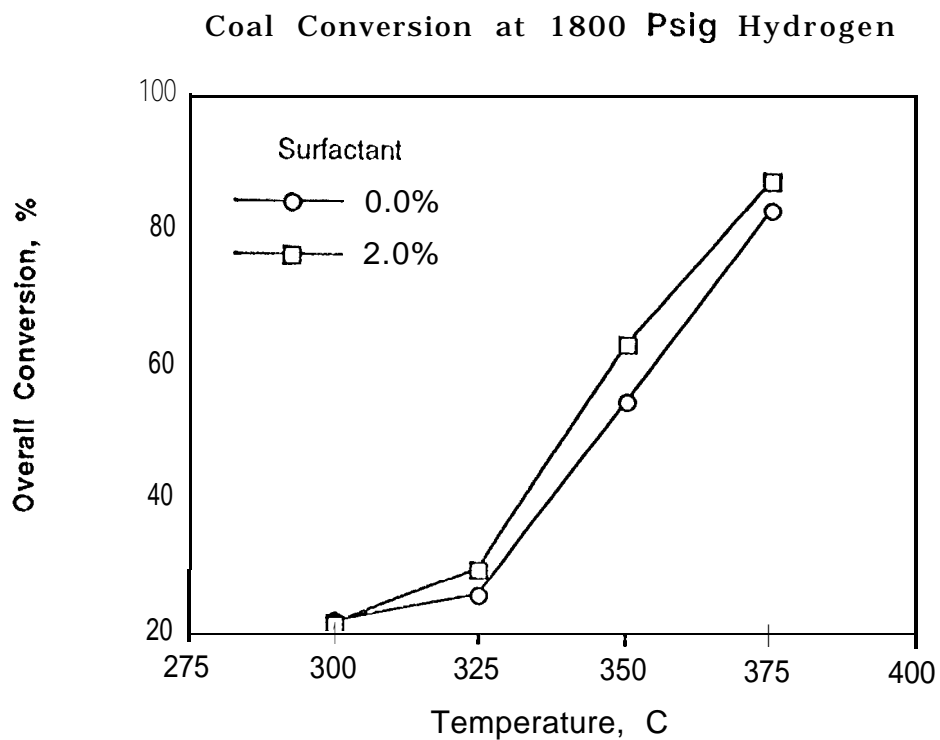


Figure 1: Temperature dependence of conversion with and without surfactant.

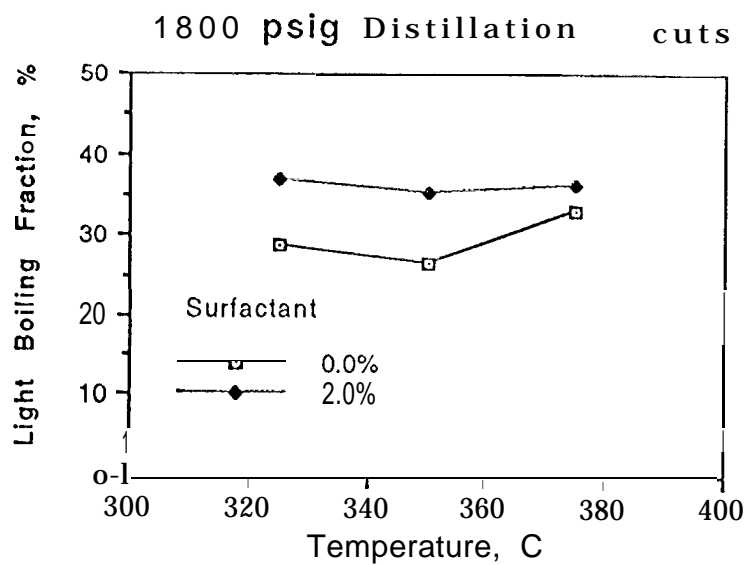


Figure 2: Temperature dependence of light boiling fractions with and without surfactant.

The increase in light boiling fractions of the filtrate, on the other hand, is significant up to 350°C only. Analytical test results on the structure and functional groups of organic compounds in the filtrate, filtercake and extracted residues show only minor differences in the samples processed with and without surfactant. The same is also true of the structure and functional groups for the successive extracts obtained by washing the filtercakes with hexane, toluene, and THF. The most significant differences obtained for the hexane and THF extracts are in the average molecular weights, which were higher in the 375°C processing run with 2.0 % surfactant than for the case with no surfactant added.

The above results suggest that this surfactant appears to speed up the breakage of the crosslinks in the coal. If this process was rate controlling, the reaction of the hydrogen with coal fragments and the rehydrogenation of the solvent, would also speed up. The following discussion will help visualize how the surfactant may help in the breakage of the crosslinks of the coal. Let the coal be represented by R-O-H. Without the surfactant, coal molecules (represented as R-O-H and R'-O-H in Figure 5) are associated by hydrogen bonding between the H-atom of one coal molecule and the O-atom of the other (dashed line). Due to its anionic polar nature, the surfactant attaches itself to the acid site (H atom) on the coal. Thus it breaks the association with the O-atom between different coal molecules, increasing the

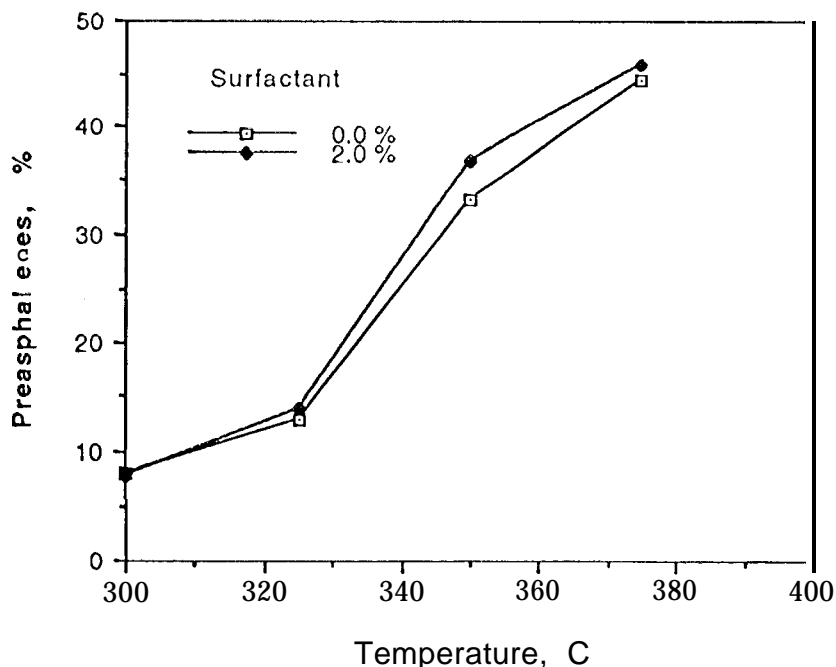


Figure 3: Yield of preasphaltenes (as determined from THF extraction) as a function of temperature with and without surfactant.

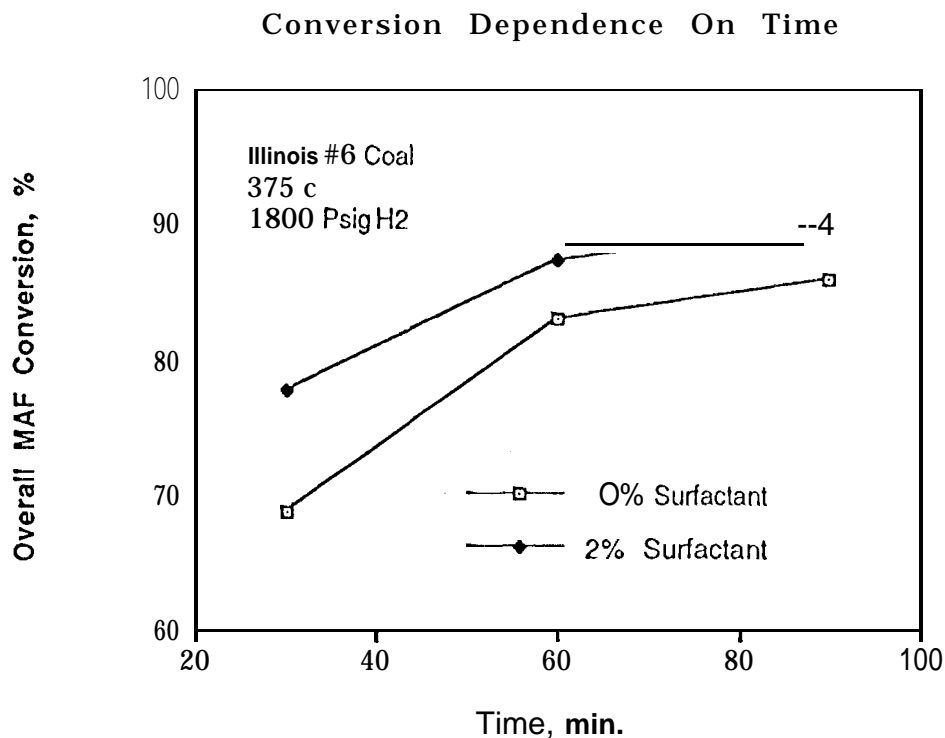


Figure 4: Conversion dependence on time, with and without the addition of surfactant.

favorable hydrogenation reactions. Because the lignosulfonate is a Lewis acid and a partially hydrogenated aromatic compound, it is possible that it could act as a hydrogen donor in the reaction. This is a possible additional avenue of increase in favorable liquefaction **processes due to the** surfactant.

The addition of the surfactant at 375 °C processing temperature increased coal conversion from 83% to about 88%. The increase was primarily related to the increase in the THF extracted species from the filtercakes in agreement with the results in Figure 3. As the THF extracted species are expected to be preasphaltenes and the GC/MS analysis indicates these species to be polyaromatic compounds, the increase in the average molecular weight of the THF extract was not surprising. The species that converted to a THF soluble product due to the surfactant are expected to be bigger (hence, higher molecular weight) than those that did not require the surfactant.

The effects of the surfactant on the quality of the filtrate (i.e. the fraction of light boiling distillates) are clearly dependent on processing temperature. The surfactant increases the straight chain (lower boiling) hydrocarbons as well the molecular weight of the polyaromatics. At 350°C, the increase in straight chain hydrocarbons based on FTIR, appears to dominate, resulting in an increase of lighter fractions. At 375 °C, the production of aromatics appears to counter the production of aliphatic hydrocarbons. Hence, a significantly smaller increase in lighter fractions is observed.

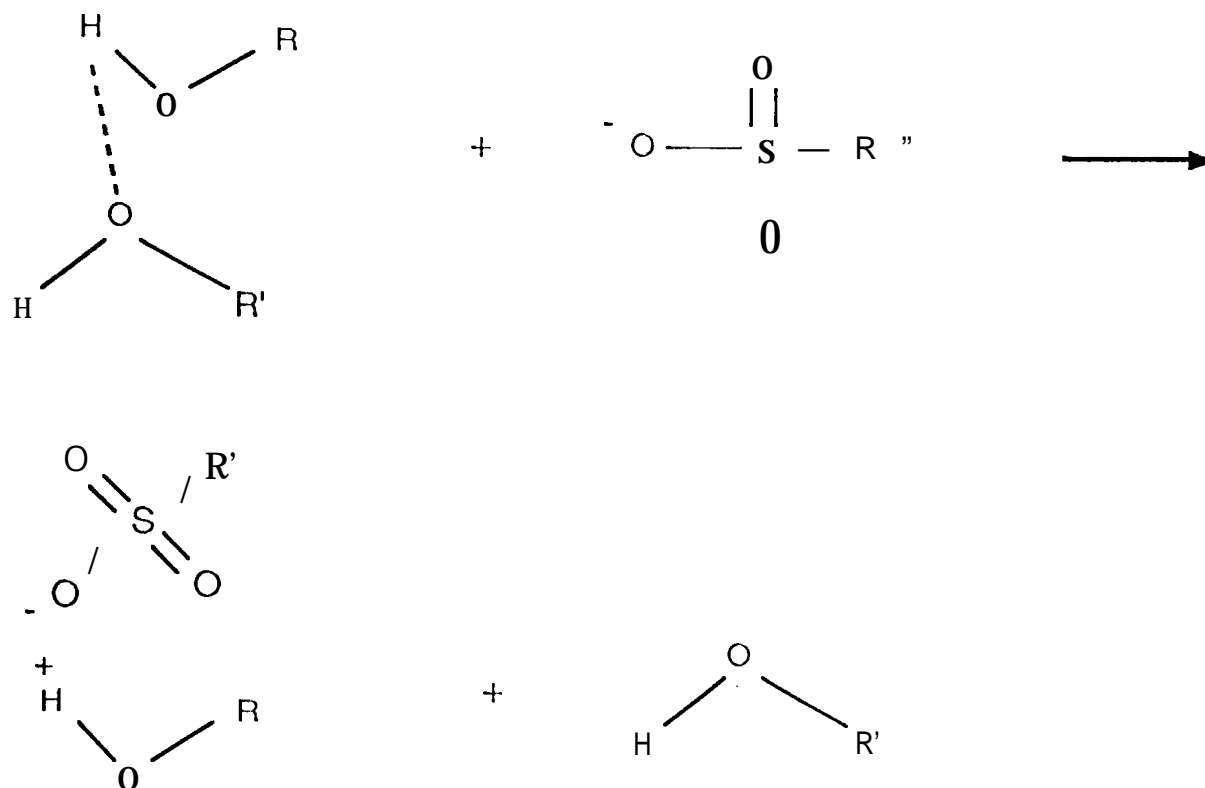


Figure 5: Representative mechanism for the role of the surfactant.

The observed increase in the overall coal conversion due to the addition of the surfactant, sodium lignosulfonate, appears to result mainly from the breakage of crosslinks of the associated coal molecules. This, in turn, appears to lead to greater access of hydrogen to the coal fragments and thus a significant increase in the hydrogenation rate and subsequent solubilization rate. Table 1 shows that overall conversions are relatively independent of surfactant concentration change from 0.5 to 2.0 %. The observation that overall coal conversions are relatively independent of surfactant concentration is consistent with a recent study on the kinetics of adsorption of surfactants on mineral matter. Marbrel and Somasundaran⁷ have reported a study of the surfactant adsorption on a mineral at the solid-liquid interface by electron spin resonance spectroscopy. This study showed that 40% of the total ultimate surfactant adsorption occurred during the first 5 seconds of contact independent of the initial surfactant concentration (provided sufficient surfactant was present). The second stage of adsorption was much slower and occurred on the order of one to three hours. In our case, where the coal is a solid with preferential acid sites for the surfactant, close to 100% of the total surfactant adsorption may take place during the first minute of contact, even with very low surfactant concentrations.

The use of a surfactant in coal liquefaction reactors can be utilized in a process that requires less intensive processing conditions that approach the conversion of the catalytic process. The state-of-the-art catalytic process utilizes a two-stage ebullated bed catalytic reactor with operation temperatures of 425 °C and 440 °C respectively and 2200 psig hydrogen pressure. The present work implies that an alternative

thermal process may be competitive using a low cost disposable surfactant at lower temperature and pressures instead of an expensive solid supported catalyst. This would allow for lower initial capital and operational costs. A further detailed economic analysis is warranted.

Conclusions

The addition of sodium lignosulfonate surfactant has been shown to increase the conversion of coal in batch coal liquefaction experiments in the temperature range from 300 to 375 °C. This increase in conversion was associated with an increase in less than 300 °C boiling point distillate over process runs without surfactant. The improvement in conversion by the addition of surfactant is believed to result from decreasing the agglomeration of the coal and increasing the rate of breaking crosslinks in the coal into smaller molecular units. These results imply the possibility of improved process economics for coal liquefaction by being able to have liquefaction unit operations at lower temperature and pressures than the conventional catalytic process and eliminating the need for a costly catalyst.

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Acknowledgment

The research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of *Technology*, under contract with the National Aeronautics and Space Administration. The work was sponsored by the Pittsburgh Energy Technology Center, Department of Energy, through DOE/NASA Interagency Agreement No. DE-A122-92PC921 50.